[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Isomerization of Some α-Hydroxysilanes to Silyl Ethers. II[1]

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Representative members of all possible types of alkyl and aryl α-silylcarbinols were treated with sodium–potassium alloy in ether at room temperature. It was found that all of these compounds, with the exception of the primary carbinol, triphenylsilylmethanol, were readily rearranged to the isomeric silyl ether in good yield. A number of new compounds are reported.

Recently we reported that aryl or mixed aryl-alkyl α-silyldiphenylcarbinols could be isomerized to the corresponding silyl ethers either by sodium–potassium alloy, boiling pyridine or with alkali.[2]

$$\mathrm{RPh_2Si{-}COHPh_2} \longrightarrow \mathrm{RPh_2Si{-}OCHPh_2}$$
$$\mathrm{R = Ph\ or\ Me}$$

Further investigation has shown, contrary to opinion expressed,[2] that this reaction occurs with a wide variety of α-silylcarbinols and is not restricted to the diphenylcarbinols. Indeed all aliphatic, aromatic and mixed aliphatic-aromatic secondary or tertiary α-silylcarbinols investigated were found to be fairly readily converted to the isomeric silyl ether using traces of sodium–potassium alloy in ether at room temperature as the isomerizing agent. Table I summarizes the compounds investigated to date, the conditions of isomerization and the yield of silyl ether obtained and the melting points of all materials.

TABLE I

ISOMERIZATION OF α-SILYLCARBINOLS TO SILYL ETHERS WITH NA/K ALLOY

Silylcarbinol	M.p., °C.	Time	Ether yield, %	M.p., °C.
$Ph_3SiCOHPh_2$	156–159	3 min.	95	83–84
$Ph_3SiCOHMePh$	120–122	18 hr.	67	48–49
$Ph_3SiCOHPhH$	116–117	1 hr.	65	84.5–85.5
$Ph_3SiCOHMe_2$	155–156	18 hr.	33[a]	88–89
$Ph_3SiCOHMeH$	101–101.5	4.5 hr.	67[b]	64–65
Ph_3SiCH_2OH	116–117	3–18 hr.	Nil[c]	
$Ph_2MeSiCOHPh_2$	127.5–128	1 hr.	86	72–72.7
$Me_3SiCOHPh_2$	57.7–59.2	1.5 hr.	60	[d]
$(Ph_3Si)_2COHMe$	212–214	143 hr.	82	156–157.5

[a] Also isolated was 16% triphenylsilanol, m.p. 150–151°. [b] Also isolated was 11% of 1-triphenylsilyl-1-triphenylsiloxyethane, m.p. 156–157°. [c] 30–70% of starting material recovered along with traces of unidentified high-melting product but no triphenylmethoxysilane found. [d] B.p. 124–124.5° (2 mm.), n^{20}_D 1.5265, d^{28} 0.993.

Two general effects may be noted from these results. Although we have not quantitatively investigated the rates of isomerization and the times noted above are not necessarily accurate criteria of the rates of reaction, it was found generally that as the groups attached to the carbinol carbon were changed from aryl to alkyl or hydrogen, the reactions became slower and more difficult to accomplish under these conditions as indicated by increased reaction times and decrease in yield. In the extreme where both groups were hydrogen, as in triphenylsilylmethanol, we were unable to cause rearrangement of this compound to triphenylmethoxysilane.

It was also apparent that changing the groups attached to silicon from aryl to alkyl had little effect on the reaction since good yields were obtained from triphenyl-, methyldiphenyl- or trimethylsilyl derivatives.

The preparations of the new compounds used in these studies are described in the Experimental section, but a few comments seem justified. It is interesting that the carbonyl group of triphenylsilyl phenyl ketone[3] is susceptible to reaction with methylmagnesium iodide and lithium aluminum hydride, whereas with bulkier reagents such as phenylmagnesium bromide or phenyllithium little or no reaction occurred.[3] 1,1-Bis-(triphenylsilyl)-ethanol was the main product isolated from the reaction of triphenylsilyllithium with either acetyl chloride or acetic anhydride. During the course of this work it was reported that the compound could be isomerized to 1-triphenylsilyl-1-triphenylsiloxysilane by alcoholic potassium hydroxide,[4] but no yield is reported.

During the actual rearrangements the surface of the metal frequently acquires an intense color although this color is destroyed when the reaction mixture is swirled. However toward what we believe to be the completion of the rearrangement the medium may acquire a pale color and the color on the metal surface is not dispersed by swirling. We have used this effect as a rough criterion for the time duration of the reaction. These intense colors certainly cannot be attributed to the salt of the carbinol, but they may well be due to the formation either of an organometallic or radical species on the metal surface. Were the intermediate a radical such as $R_3SiOCR_2\cdot$, it would be expected to form the silyl ether by hydrogen abstraction from the solvent. It may be significant that, when the rearrangement is carried out in carbon tetrachloride where no hydrogen is available for abstraction, rather than in ether, no rearrangement occurs even over prolonged reaction periods, although admittedly the surface of the alloy appears to become coated, so that reaction may be prevented. A mechanism for these rearrangements has previously been proposed[2] and will not be elaborated on further at this time. Additional results appear to conflict with the original proposal and the mechanism of the rearrangement is being actively investigated.

In some reactions a slight evolution of hydrogen and the concomitant formation of an ether-insoluble precipitate, presumably the salt of the carbinol, was observed. On one occasion, with

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(1) Presented in part at the 41st Annual Conference of the Chemical Institute of Canada at Toronto, Canada, May, 1958.

(2) A. G. Brook, THIS JOURNAL, **80**, 1886 (1958).

(3) A. G. Brook, *ibid.*, **79**, 4373 (1957).

(4) D. Wittenberg and H. Gilman, *ibid.*, **80**, 4529 (1958).

triphenylsilyldimethylcarbinol, a low yield of triphenylsilanol was obtained along with a low yield of the isomerized compound. We have found that silyl ethers are sensitive to cleavage by sodium-potassium alloy, which accounts for the isolation of this compound.

Evidently virtually all α-silylcarbinols can be expected to be rearranged to the corresponding ethers fairly readily, particularly in the presence of an alkali metal. Hence the attempted formation of these compounds by reaction of an organosilylmetallic reagent with a carbonyl compound should be immediately suspect and the product carefully examined to establish whether the carbinol or the isomeric ether was actually obtained. It has already been observed that reaction of triphenyl-, methyldiphenyl- and dimethylphenylsilylmetallics with benzophenone give the isomerized ether[5a,b] although the first of these reagents adds to the carbonyl group of formaldehyde,[6] acetone[2] and acetaldehyde to give the normal unrearranged carbinol.

It is doubtful whether the rearrangement reported here will have much synthetic application since in general silyl ethers are much more readily prepared than are the corresponding α-silylcarbinols.

Experimental[7]

Triphenylsilylmethylphenylcarbinol.—Treatment of triphenylsilylphenyl ketone with an equivalent of methylmagnesium iodide gave an 85% yield of the carbinol, m.p. 120–122°, after recrystallization from benzene petroleum ether (b.p. 90–100°).

Anal. Calcd. for $C_{26}H_{24}OSi$: Si, 7.37. Found: Si, 7.46.

Triphenylsilylphenylcarbinol.—Treatment of triphenylsilyl phenyl ketone with excess lithium aluminum hydride in ether gave 81% of the carbinol, m.p. 116–117°, after recrystallization from petroleum ether (b.p. 90–100°). The infrared spectrum showed normal OH absorption.

Anal. Calcd. for $C_{25}H_{22}OSi$: Si, 7.66. Found: Si, 7.73.

Triphenylsilylmethylcarbinol.—To a solution of 50 ml. (0.0193 mole) of triphenylsilyllithium in tetrahydrofuran, prepared from 5.0 g. (0.00965 mole) of hexaphenyldisilane, was added 2 ml. (0.035 mole) of acetaldehyde in 50 ml. of tetrahydrofuran. The reaction was slightly exothermic and the dark color of the silylmetallic faded as the acetaldehyde was added. After about 10 min. Color Test I was negative. The reaction was worked up essentially as above, and yielded a colorless oil on evaporation which crystallized on scratching. Recrystallization from petroleum ether (b.p. 60–70°) and then ethanol gave 3.14 g. (53%) of white crystalline triphenylsilylmethylcarbinol, m.p. 101–101.5°, whose infrared spectrum showed absorption characteristic of an OH group.

Anal. Calcd. for $C_{20}H_{20}OSi$: Si, 9.21. Found: Si, 9.03.

Benzhydryltrimethylsilane.—To 172 ml. of 1.45 *N* (0.25 mole) of *n*-butyllithium in ether was added 42 ml. (0.25 mole) of diphenylmethane in 150 ml. of ether. The solution was refluxed for 24 hr. and then 30.7 ml. (0.24 mole) of trimethylchlorosilane was added. The red-brown color rapidly faded through yellow to a pale chocolate color and a precipitate formed. The mixture was stirred 16 hr. by which time Color Test I was negative. The reaction mixture was poured into dilute acid, ether extracted, dried, and distilled under reduced pressure and after removing a large forerun containing much diphenylmethane and some crystalline material, a 29.1 g. (48.5%) fraction, b.p. 154–165° (16 mm.), was collected which solidified. This was recrystallized from ethanol to yield white benzhydryltrimethylsilane, m.p. 73–75°.

Anal. Calcd. for $C_{16}H_{20}Si$: C, 79.9; H, 8.33. Found: C, 79.4; H, 8.11.

Bromobenzhydryltrimethylsilane and Trimethylsilyldiphenylcarbinol.—To 14.88 g. (0.062 mole) of benzhydryltrimethylsilane in 150 ml. of carbon tetrachloride was added 11.0 g. (0.062 mole) of N-bromosuccinimide and a trace of benzoyl peroxide. The mixture was refluxed for 16 hr. and then cooled. The succinimide was filtered off, and the filtrate evaporated under reduced pressure to yield an oil. This bromobenzhydryltrimethylsilane could be distilled at 148–150° (1.2 mm.) to give a pale yellow liquid, not further characterized, other than to show it contained bromine. Instead the crude oil above was dissolved in 150 ml. of acetone and 25 ml. of water and 10.4 g. (0.062 mole) of silver acetate was added. An apparently rapid reaction occurred with the production of considerable heat and the formation of a pale yellow precipitate. The reaction mixture was stirred for about 14 hr. in the dark and the precipitate was then filtered off. The filtrate was drowned in about a liter of water and was thrice extracted with chloroform. The chloroform extracts were dried over sodium sulfate, and on removal of the chloroform under reduced pressure a white solid, m.p. 52–55°, was formed. Recrystallization from petroleum ether (b.p. 60–70°) yielded 10.24 g. (65%) of white trimethylsilyldiphenylcarbinol, m.p. 57.7–59.2°.

Anal. Calcd. for $C_{16}H_{20}OSi$: C, 74.97; H, 7.81. Found: C, 74.78; H, 7.85.

1,1-Bis-(triphenylsilyl)-ethanol.—To 3.06 g. (0.030 mole) of redistilled acetic anhydride in 50 ml. of tetrahydrofuran at −70° was added over 0.5 hr. 50 ml. (0.0193 mole) of triphenylsilyllithium in tetrahydrofuran, prepared from 5.0 g. (0.00965 mole) of hexaphenyldisilane. The reaction mixture became a light reddish-brown color and when the addition was complete Color Test I was negative. The reaction mixture was drowned in dilute acid and ether extracted. Evaporation under reduced pressure gave 6.1 g. of white solid. Several recrystallizations of this material from chloroform and chloroform-ethanol eventually gave 1.75 g. (39%) of white crystalline 1,1-bis-(triphenylsilyl)-ethanol, m.p. 212–214°, and after several recrystallizations 0.5 g. (3%) of 1-triphenylsilyl-1-triphenylsiloxyethane, m.p. 156–157°, identified by mixed melting point with an authentic specimen, and other products which will be described elsewhere.[8] Similar results were obtained with acetyl chloride.

Anal. Calcd. for $C_{38}H_{34}OSi_2$: Si, 9.96. Found: Si, 10.01.

Preparation of Silyl Ethers. A. Sodium Salt Method. Methylphenylmethoxytriphenylsilane.—To 40 ml. (0.3 mole) of redistilled α-methylbenzyl alcohol was added 2.3 g. (0.1 g. atom) of sodium and 200 ml. of dry benzene. After about 2 hr. the sodium had completely reacted and 29.6 g. (0.1 mole) of triphenylchlorosilane was added. The mixture was refluxed for 3 hr. during which time a precipitate formed. On cooling some crystals deposited. These and the original precipitate (NaCl) were filtered off, washed with water to remove the salt, and the insoluble material (9.0 g., 37%) was shown to be hexaphenyldisiloxane by its m.p. 218–221° and mixed melting point with an authentic specimen.

The filtrate was concentrated under reduced pressure to yield an oil which was distilled. After a forerun of 24 ml. of α-methylbenzyl alcohol, b.p. 63° (1.5 mm.), a total of 21.1 g. (55%) of oil, b.p. 202–204° (1.0 mm.), was collected, n^{20}_{D} 1.6060, which crystallized after standing one month. Recrystallization from ethanol gave white, solid methylphenylmethoxytriphenylsilane, m.p. 48–49°.

Anal. Calcd. for $C_{26}H_{24}OSi$: Si, 7.37. Found: Si, 7.65.

The infrared spectrum showed absorption characteristic of an Si–O linkage. This material was shown to be identical with that produced by rearrangement of triphenylsilylmethylphenylcarbinol, which had m.p. 47–49°, b.p. 200–204° (1 mm.), n^{20}_{D} 1.6054. Other silyl ethers produced by essentially the above method were: benzyloxytriphenylsilane, 51% yield, m.p. 84.5–85.5°, recrystallized from petroleum ether (b.p. 60–70°) (*Anal.* Calcd. for C_{25}-

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(5) (a) H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2935 (1953); (b) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 607 (1958)

(6) H. Gilman and T. C. Wu, *ibid.*, **76**, 2502 (1954).

(7) Reactions involving organometallic reagents were carried out in an atmosphere of dry, oxygen-free nitrogen.

(8) H. Gilman, personal communication.

$H_{22}OSi$: Si, 7.66. Found: Si, 7.70); isopropoxytriphenylsilane, 67% yield, m.p. 88–89°, recrystallized from isopropyl alcohol (*Anal.* Calcd. for $C_{21}H_{22}OSi$: Si, 8.81. Found: Si, 8.87). The infrared spectrum of these compounds was consistent with their proposed structures.

B. Pyridine Method. **Benzhydryloxytrimethylsilane.**—To 18.5 g. (0.10 mole) of recrystallized benzhydrol in 25 ml. of pyridine and 30 ml. of dry xylene was added dropwise over 0.5 hr. 12.8 ml. (0.10 mole) of trimethylchlorosilane. Shortly after addition was started a precipitate formed and the reaction mixture became warm. After the addition was complete the reaction mixture was refluxed for 0.5 hr. which resulted in the precipitate melting and two liquid phases being present. On cooling one liquid phase resolidified. The precipitate (pyridine hydrochloride) was filtered off and the filtrate was drowned in dilute acid. This mixture was extracted several times with benzene and back-extracted with dilute acid. After drying, the benzene layer was concentrated under reduced pressure to yield an oil which was distilled. After a small forerun a total of 18.9 g. (81%) of colorless benzhydryloxytrimethylsilane, b.p. 124–124.5° (2.0 mm.), was isolated, $n^{20}D$ 1.5265, d^{28} 0.993.

Anal. Calcd. for $C_{16}H_{20}OSi$: C, 74.97; H, 7.81. Found: C, 75.18; H, 7.85.

This material was shown by its infrared spectrum to have an Si–O linkage and was identical with material obtained by the isomerization of trimethylsilylphenylcarbinol, b.p. 116° (1 mm.), $n^{20}D$ 1.5264, d^{28} 0.993.

Similarly prepared was 1-triphenylsilyl-1-triphenylsiloxyethane, m.p. 156–157°, 20% yield, starting with triphenylsilylmethylcarbinol and triphenylchlorosilane.

Isomerizations of α-Silylcarbinols of Silyl-ethers.—All rearrangements were carried out in essentially the same way. The yields obtained are reported in Table I. In each case infrared spectra of the isomerized material and the authentic silyl ether were compared and found to be the same. In addition, where applicable, mixed melting points were taken to establish the identity of the materials. The following are typical of the procedures used; see also reference 2.

Isomerization of Methyldiphenylsilyldiphenylcarbinol to Benzhydryloxymethyldiphenylsilane.—To 1.0 g. (0.0026 mole) of the carbinol in 20 ml. of dry ether was added 4 drops of 1:5 sodium–potassium alloy. The surface of the metal soon became blue but no hydrogen evolution was observed. When the mixture was swirled the blue color momentarily disappeared. After 1 hr. the mixture was slightly cloudy and yellow. The ether solution was decanted off the alloy into dilute hydrochloric acid and the material was ether extracted, and then dried over anhydrous sodium sulfate. The ether solution was evaporated under reduced pressure to yield an oil which completely crystallized when seeded with authentic benzhydryloxymethyldiphenylsilane. This 0.91 g. (91%) of material was recrystallized from petroleum ether (b.p. 60–70°) to yield 0.86 g. (86%) of the ether, m.p. 71–72°, identified by mixed melting point with an authentic specimen.

Isomerization to Triphenylsilyldimethylcarbinol to Isopropoxytriphenylsilane.—To 0.8 g. (0.0025 mole) of the carbinol in 30 ml. of dry ether was added a few drops of sodium-potassium alloy. The surface of the alloy became yellow and overnight the entire medium became pale yellow. The ether solution was decanted into dilute acid which was ether-extracted. Evaporation gave a gummy solid which was recrystallized from petroleum ether (b.p. 60–70°) to give 0.11 g. (16%) of triphenylsilanol, m.p. 150–151°, identified by mixed melting point, and 0.26 g. (33%) of isopropoxytriphenylsilane, m.p. 87–89°, identified by mixed melting point with an authentic specimen.

Miscellaneous Rearrangements.—During an attempt to oxidize triphenylsilylphenylcarbinol back to triphenylsilyl phenyl ketone by the Oppehauer method the compound was rearranged in good yield to benzyloxytriphenylsilane. Thus 0.20 g. (0.00054 mole) of the carbinol, 20 ml. of acetone, 20 ml. of benzene and 0.22 g. (0.0011 mole) of aluminum isopropoxide were refluxed for 24 hr. On work-up there was isolated 0.19 g. (95%) of crude benzyloxytriphenylsilane, m.p. 64–79°, which after recrystallization from petroleum ether (b.p. 90–100°) gave 0.13 g. (65%) of pure silyl ether, m.p. 81–83°, identified by mixed melting point with an authentic specimen.

It was also observed that the rearrangement of 1,1-bis-(triphenylsilyl)-ethanol occurred with difficulty in ether but not at all in tetrahydrofuran. Thus when 1.0 g. (0.0018 mole) of the carbinol in 40 ml. of tetrahydrofuran was treated with a few drops of Na/K alloy over 20 hr. the medium became a deep red-green color. Work-up as usual gave 1.0 g. of gummy solid, which on crystallization from petroleum ether (b.p. 90–100°) gave 0.3 g. (31%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point, and 0.12 g. of an unidentified white solid, m.p. 210–214°, shown not to be hexaphenyldisiloxane or starting material by mixed melting point.

When this procedure was repeated using, instead of tetrahydrofuran, 100 ml. of a 1:3 benzene–ether mixture (required to dissolve the compound) work-up after 143 hr. gave 0.70 g. (70%) of 1-triphenylsilyl-1-triphenylsiloxyethane, m.p. 155–156.5°, identified by mixed melting point and 0.12 g. of crude material, m.p. 120–145°.

Cleavage of Benzhydryloxytriphenylsilane by Alloy.—Treatment of 1.5 g. (0.0034 mole) of benzhydryloxytriphenylsilane with 0.5 ml. of sodium–potassium alloy in 25 ml. of ether over 16 hr. gave initially a green-yellow color on the metal surface which changed to deep blue. Eventually the entire medium became blue and at the end of the reaction no alloy remained, Work-up gave 0.64 g. (64%) of triphenylsilanol, m.p. 151–152°, identified by mixed melting point and the mother liquors gave a positive 2,4-dinitrophenylhydrazine test for benzophenone.

Attempted Rearrangement of Triphenylsilyldiphenylcarbinol in Carbon Tetrachloride.—When triphenylsilyldiphenylcarbinol (0.5 g.) in 10 ml. of purified carbon tetrachloride was treated over 10 min. with a few drops of sodium–potassium alloy as usual, no color formed on the alloy surface although it appeared to develop a gray coating. Work-up gave 0.42 g. (84%) of recovered carbinol, m.p. 155–157°.

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